PREPARATION OF COMPOSITE POWDERS BY ELECTROLESS PLATING
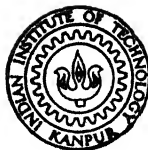
By

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JANUARY, 1977

PREPARATION OF COMPOSITE POWDERS BY ELECTROLESS PLATING

A Thesis Submitted
In Partial Fulfilment of the Requirements
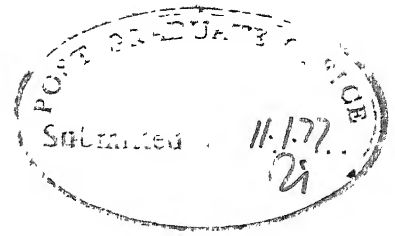for the Degree of
MASTER OF TECHNOLOGY

By
R. K. KAUL

to the

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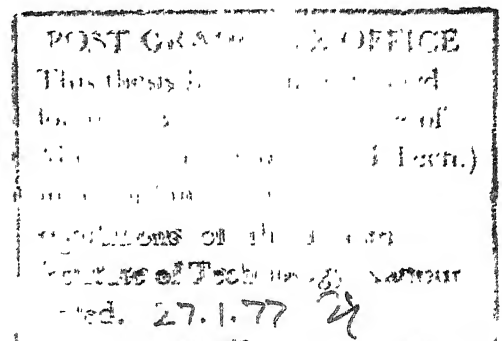ME - 1977 - M - KAU . PRE

CERTIFICATE

Certified that the work "Preparation of Composite Powders by Electroless Plating" has been carried out under my supervision and the same has not been submitted elsewhere for a degree.

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SYNOPSIS

Composite powders (alumina/Ni, WC/Co, W/Ni and Cu/Ni) are prepared by coating metals (Ni and Co) onto alumina, WC, W and Cu by a chemical reduction process, known as electroless plating, using strong reducer (sodium hypophosphite).

The effect of plating time on various properties, like wt. % nickel or cobalt coated, flow rate, apparent density, have been studied to arrive at optimum conditions to obtain desired composite powders. Sintering experiments have also been carried out for Cu/Ni and W/Ni composite powders.

CHAPTER 1

INTRODUCTION

The term "Composite" usually designates a combination of materials which form neither alloys nor intermetallic compounds. This includes both metal-metal and metal-nonmetal combinations. In discussion of powders, however, the term refers only to combinations of two metallic phases within each particle.

Composite powders usually consist of so-called "coated" powder particles. Each individual particle consists of a core of one particular metal or nonmetal surrounded by a shell of another metal. The two metals may or may not combine to form an alloy or an intermetallic compound.

· Many processes are available for the preparation of composite powders, such as the thermal decomposition of metal carbonyls, the displacement reactions involving surface diffusion, the hydrogen reduction of volatile compounds and liquid-phase deposition involving electroless and Sherritt-Gordon processes.

The advantage of composite powders lies in overcoming many of the problems associated with the compacting and sintering of powder mixtures. It has been found that the components in the composite powder compacts are better

dispersed than can be obtained in conventional mixed powder compacts. The achievement of more rapid alloying by diffusion in composite powder compacts has been attributed to better mechanical dispersion of the components, greater protection of reactive elements against oxidation or other reactions at elevated temperatures, and more intimate contact between the components over a greater surface area than is possible in mixed powder compacts. Liquid-phase sintering of compacts is possible without large-scale expansion of the compacts, by coating low melting point core particles with a high melting point material (e.g. Ni/Cu composites).

CHAPTER 2

REVIEW OF LITERATURE ON THE TECHNOLOGY

OF COATED POWDERS

The technology of production and usage of metal
powders is about fifty years old. Now it has gained popul-
arity in the fields like nuclear technology, gas turbine
engineering, and aerospace applications. In response to
these demands a new technology of coated powders has been
developed.

There is little literature available about it.
The technology of composite powders has been discussed here
from the standpoints of methods of preparation, properties,
and applications.

2.1 Methods of Preparation:

Classification of production of composite powders
is done on the basis of whether the deposition takes place
on the core particles from

2.1.1 The vapour phase

2.1.2 The liquid phase or

2.1.3 The solid phase.

Within these three general groupings there are
two subdivisions according to whether the material being

deposited is:

A. An element or

B. A compound.

2.1.1 Vapour Phase Deposition:

A. Element Deposition: There are three general types of reactions by which the elements can be deposited on the powder substrate

  (i) Thermal decomposition

 (ii) Displacement reactions

(iii) Hydrogen reduction.

(i) Thermal Decomposition[1]: This method consists in choosing such a compound, of the element to be coated, that can be vapourised and decomposed easily, on the powder substrate at high temperatures. The volatile metal compounds which can be thermally decomposed to yield metal include the hydrides, halides, carbonyls and some organo-metallic compounds. The hydrides can be used to deposit boron, silicon, germanium, arsenic, antimony and bismuth. Carbonyls of iron, cobalt, nickel, chromium, molybdenum and tungsten can be utilized to give metal by thermal decomposition. For example nickel carbonyl vapour decomposes into carbon monoxide and metallic nickel which gets deposited upon the powder substrate.

$$Ni(CO)_4 \xrightarrow{330°F} Ni + 4CO.$$
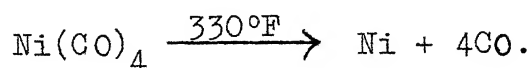
In 1951 Cline and Wulff[2] coated various ceramic powders with nickel by this reaction. The carbonyl halides, especially the carbonyl chlorides, of copper, gold and the platinum group metals can be thermally decomposed to deposit the metal.

$$Pt(CO)_2Cl_2 \longrightarrow Pt + 2CO + Cl_2 \; .$$
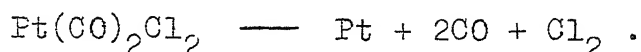
(ii) <u>Displacement Reaction</u>: In this method the metal bearing vapours are made to come in contact with the core particles. The core particle material gets displaced by the metal from the vapour. The metal thereupon deposits upon the core particles while the displaced core particle material is swept away in the gas steam. These reactions are carried out at temperatures high enough that diffusion supplies base material to the surface at rates sufficient to maintain the reaction. Iron and steel can be coated with chromium, aluminum, silicon, boron, titanium, vanadium, niobium, antimony, cerium, manganese, zinc, tin, molybdenum and tungsten alloys.

Since this is a diffusion controlled process, which is necessary for the reaction to occur, these coatings are not strictly elemental in nature. Surface layers are rich in deposited material and goes on decreasing as we move in. We do not get sharp discontinuity.

(iii) <u>Hydrogen Reduction</u>: A mixture of hydrogen and metal halide vapour is mixed at the surface of the material to be

coated. The temperature is so adjusted that the reduction
can take place. This method is of wide application because
of the readily available metal-halides and their volatility.
For example tungsten chloride vapour is reduced by hydrogen
to tungsten metal.

$$WCl_6 + 3H_2 \rightarrow W + 6HCl$$
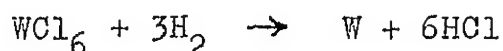
Possible metals which can be coated by this method are boron,
silicon, titanium, zirconium, vanadium, niobium, tantalum,
chromium, molybdenum, tungsten, iron, cobalt, nickel,
germanium, tin, arsenic, antimony and bismuth. By this
method we can also deposite metal alloys on the powders, by
using more than one metal-halide vapour simultaneously.

B. <u>Compound Deposition</u>: In case of graphite powder if the
deposition of metal is at high temperature either by thermal
decomposition or by hydrogen reduction, the metal carbide
may also be produced. Based on the same principle we can
coat uranium dioxide fuel element with alumina or beryllia.

Fluidization of the powder during coating is
necessary to coat each particle of the powder. In this case
it is done either by fluidized bed technique using the
reacting vapour as the fluidizing gas or sometimes by
mechanical stirring or agitation of the powder bed.

Complications in vapour phase deposition: (a)
there may be problems of the powder bed sintering together

during coating. Some workers encountered sintering problems when attempting to carry out iron coatings via hydrogen reduction of the chloride at 1200°F. (b) Problems may arise from undesired reactions between the powder substrate and the depositing vapour. Cline and Wulff[2] failed to deposit molybdenum, via hydrogen reduction of the pentachloride, upon titanium carbide powders. It was found that the titanium carbide reacted to form titanium tetrachloride which got volatilized at the temperature employed.

2.1.2 Liquid Phase Deposition:

In liquid phase deposition the metal is deposited by reduction of the metal ions in an aquous metal salt solution by any of the following techniques:

  (i) Hydrogen reduction

 (ii) Electroplating

(iii) Electroless plating

 (iv) Chemical precipitation.

(i) Hydrogen Reduction: In this process ammonical metal salt solution is reduced to metallic form by the application of hydrogen under high pressure and temperature. The reaction is as follows:

$$M^{++} + H_2 \rightarrow M + 2H^+$$

The coating on various core particles is carried out in 4, 12, or 100 litre autoclaves at elevated temperatures and pressures. The autoclave is charged with the core and the metal solution and then sealed and heated to the desired temperature under hydrogen pressure. The time of completion of the reduction varies from 5 to 60 minutes, depending upon the operating conditions and the catalytic activity of the core material.

Sherritt Gordon Mines Limited[3,4,5] has deposited pure nickel upon powders. They have taken ammoniacal solution of nickel ammonium sulphate, reduced to metallic nickel by the application of hydrogen at 350-400°F in autoclaves using gas pressure of about 350 psig. The powders to be coated are suspended in the solution by mechanical agitation. Complete and uniform coverage of Ni is obtained

$$NiSo_4 + 2NH_3 + H_2 \rightarrow Ni^\circ + (NH_4)_2So_4$$
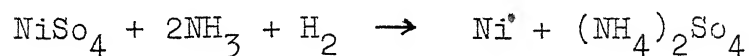
Following are the metals which can be coated on powder substrate i.e. Ni, Co, Cu and Ag. In other cases we do not get as complete or as uniform coating, on the base material, as is the case with nickel coatings. It must be taken care of that the powder, to be coated, must not react with the solution at high temperatures.

(ii) <u>Electroplating</u>: Many metals are deposited from solution by electrolysis. Paper published by Salt[6] gives

the technique of electrodeposition of an adherent coating onto stainless steel powder.

This method requires that electrical contact be made with the substrate material being coated. Which becomes difficult in case of powder substrates and is applicable only to electrically conductive powders. Hence very little work has been published upon such applications.

(iii) <u>Electroless Plating</u>: Here, a suitable buffer solution of the element to be coated, is mixed with a reducing solution. These solutions interact to cause the controlled precipitation of the "metal-plating".

In the case of nickel the plating is not pure nickel but a nickel/phosphorus alloy which contains about 9% phosphorus. Rao and Tamhankar[7] have coated various powders like WC, Fe etc. with Ni and Co by this method.

A closely analogous series of "electroless plating" solutions can be used to deposit arsenic, cobalt, copper, gold and even, to some extent chromium.[8]

(iv) <u>Chemical Precipitation</u>: It is a method of obtaining coating of metal upon powder substrate from solution by causing a metal-containing compound to nucleate and precipitate upon the substrate. The precipitate mass can then be filtered off and the metal-containing coating converted to metal by some means such as reduction in a furnace.

The type of material precipitated as the intermediate coating is usually dictated by the chemistry of the system employed but is often a hydroxide, or basic salt or an insoluble organic salt such as an oxalate. One variation of this type of coating procedure is used by Sherritt Gordon to produce molybdenum coated powders.

$$MoO_4^{2-} + H_2 \rightarrow MoO_2 + 2OH^-$$
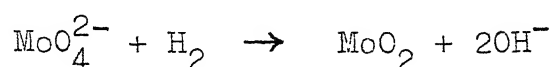
2.1.3 Solid Phase Deposition:

The applicability of solid phase deposition to the production of coated powders is very limited. Ball milling fine cobalt powder with tungsten carbide powder to produce the metal/carbide mixture which is compacted and sintered to form cemented carbide bodies. It is usually accepted that this accomplishes the smearing of the cobalt over the carbide surface and thus leads to a continuous metal network when the mixture is sintered. However, the degree of completeness or uniformity of the cobalt coverage is relatively uncontrolled in this method.

2.2 Properties:

It is difficult to generalize upon the chemistry of the composite powders as the chemistry of the two or more components of a coated powder can vary over a wide range.

These powders have some general physical charac-
teristics in common. Powder means particles lying between
.001 (1 μ) to 5 mm. The thickness of coating can also cover
the same range but usually lies between 1-100 μ with the
coating material normally representing 5-90% of the total
weight of the product. There is little literature available
about the type of bonding which occurs between the coating
and substrate powder. For high temperature deposition
reactions it is clear that some degree of diffusion must
occur at the interface. But for coatings deposited from
solutions maintained at 150-400°F it seems unlikely that any
appreciable amount of diffusion can be involved. It is
usually assumed that in these cases the main adhesive force
is "mechanical keying" of the coating to the irregularities
of the core material. The precise physical interpretation
of this is not entirely clear.

The relationship between thickness of coating and
the fraction of the total weight represented by the coating
is fixed by both the surface area of the core material and
the density ratio of the core and coating materials.

2.3 Applications:

There is a wide range of composites which can be
prepared. But, at the present, there is not an equally
wide range of applications. It seems probable that the

main fields of application for coated powders will not be as
substitutes for existing materials but that these powders
will create a new technology which is not yet fully estab-
lished. These powders can either be consolidated by pressing
and roll compacting, or can be applied by flame and plasma
spraying. The most striking applications of coated powders
are as follows:

(i) _Alloys_: Studies were made by Lund[9] on sintering and
alloying characteristics of (a) nickel-coated copper powder,
(b) copper-coated nickel powder, and (c) mixtures of nickel
and copper composite powders. He established that during
sintering the composite powders produced a compact of a much
higher density, formed alloys at a much faster rate than
mixtures of Ni and Cu powders, and did not segregate during
the processing. The alloying characteristics of Ni-Co-Cu,
Ni-Co-Mo, Ni-Co-Cr compacts prepared from composite nickel-
coated powders and mixtures of elements was studied by Lund.[10]

It is not possible to produce nickel/phosphorus
alloys, containing more than about 13% phosphorus, by conven-
tional methods i.e. adding phosphorus to molten nickel.
While by composite powder technique it is possible to
produce nickel/phosphorus alloys containing upto 30%
phosphorus.

Badia and Rohatgi[11] reported that an Al/graphite
alloy containing 2.4% C can be prepared by adding nickel/

graphite composite powders to molten Al. The utilization of graphite was 75% and 0.04% for nickel-coated and uncoated graphite respectively.

(ii) <u>Flame and Plasma Spraying</u>: Cobalt coated tungsten carbide powder is flame sprayed onto the cutting surfaces of various knives and tools. This composite powder can also be plasma sprayed. By spraying a coating of nickel clad alumina onto the surfaces of molds used in making cast iron articles it is possible to reduce greatly the wear of the molds. A problem encountered in the operation of heavy-duty stationary diesel engines is pitting of the piston crowns. This can be overcome by spray coating nickel coated alumina powder onto the piston heads. Spraying of nickel coated graphite powder yields a hard-wearing surface which also has a low coefficient of friction. This material, at present, is undergoing tests on pump shafts, bearing housings and related parts.

(iii) <u>Dispersion Strengthened Materials</u>: Composite powders are used to produce dispersion hardened alloys, like nickel coated submicron particles of various oxides. They retain their hardness at elevated temperatures. By this method , of production of dispersion strengthened materials, we can get better dispersion of the oxide particles in metal matrix than any other method of producing it.

(iv) <u>Porous Metal Strips</u>: These strips are widely used as filter media or as porous electrodes for fuel cells or nickel-cadmium batteries. These strips are usually made by the compacting and sintering of powders. Composite powders offer an alternative method for porous strip production.

(v) <u>Abradable Seals</u>: Abradable seals are used·in aircraft turbine engines. The function of the seal is to preserve the pressure differentials through the various turbine stages and in this way increase the efficiency of the engine. In order to achieve this, the seal is adjacent to the tips of the turbine blades and vanes and is located so closely that the moving blade is permitted to touch the seal and wear a path in it. The seal must be abradable, physically strong to preserve the pressure differential, and resistant to oxidation and erosion conditions. Fustukian[12] have studied the application method and properties of Ni/graphite deposits in turbine engines for abradable seal applications.

(vi) <u>Atomic Reactors</u>: In the pebble-bed reactor the fuel elements are in the form of spheres about 300 microns in diameter. The fuel bed can be completely coated with pyrolytic graphite. Graphite is used because of its high tensile strength at higher temperatures and appreciably lower neutron absorption cross-section than that of conventional cladding alloys.

An article in the Battelle Technical Review by Blocher[13] surveys the work of this group on chemical vapour deposition. The powders shown includes uranium dioxide spheres coated with alumina, beryllia, alumina upon pyro-lytic graphite and pyralytic graphite upon alumina, uranium dicarbide spheres coated with graphite and uranium mono-carbide coated with graphite. Very recently a patent was issued to Cain and Eck, assigned to the U.S.A. E.C., which disclosed the use of chromium coated uranium dioxide fuel element spheres.[14]

In the present work electroless plating method has been selected for producing the composite powders because of the following advantages of this method over the others:

(i) Coating can be done at comparatively lower temperatures,

(ii) High pressures are not required for the process as in case of hydrogen reduction method,

(iii) No electric contact is required between the powder and the electrode, as in electroplating method,

(iv) Not much sophiticated equipment is needed for the process, and

(v) More uniform coatings are generally obtainable.

CHAPTER 3

ELECTROLESS PLATING

Electroless plating was discovered by accident by Branner and Riddell[15,16] in February 1944. A number of publications and patents have appeared since that time. Despite claims in the literature, practical electroless plating process based on the use of hypophosphite have not been developed for other metals besides nickel and cobalt.
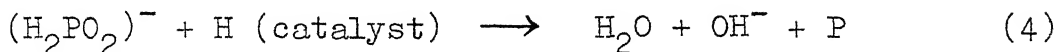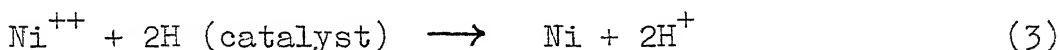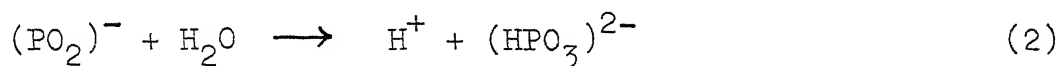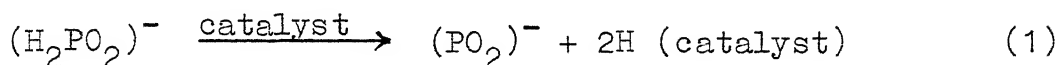
Based on certain facts, the reactions for the deposition of nickel by hypophosphite are as follows:

$$(H_2PO_2)^- \xrightarrow{\text{catalyst}} (PO_2)^- + 2H \text{ (catalyst)} \qquad (1)$$

$$(PO_2)^- + H_2O \longrightarrow H^+ + (HPO_3)^{2-} \qquad (2)$$

$$Ni^{++} + 2H \text{ (catalyst)} \longrightarrow Ni + 2H^+ \qquad (3)$$

$$(H_2PO_2)^- + H \text{ (catalyst)} \longrightarrow H_2O + OH^- + P \qquad (4)$$

$$2H \text{ (catalyst)} \longrightarrow H_2 \qquad (5)$$
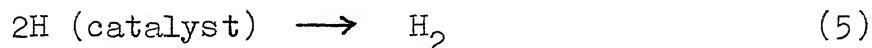
Reaction (1) expresses the fact that hypophosphite anions are dehydrogenated catalytically to metaphosphite ions. The abstracted hydrogen, either in the atomic or in any "activated" form, is absorbed on the catalyst (which could be, at that stage, considered a "hydride" in the broadest sense).

Reaction (2) shows that the metaphosphite ion reacts with water to form orthophosphite anion. It should be noted that this equation implicitly indicates the formation of hydrogen ions, as already mentioned, which explains the pH dependency of reactions (1) and (2). Reactions (1) and (2) are, of course, simultaneous.

Reaction (3) represents the reduction of nickel ions to metallic nickel by active hydrogen atoms adsorbed on the catalytic surface, with formation of hydrogen cations.

Reaction (4) represents symbolically the dehydration-reduction of hypophosphite to active phosphorus, which combines with nickel to form a nickel-phosphorus alloy.

Reaction (5) represents the formation of molecular (gaseous) hydrogen.

It can be seen that reactions (1) and (2) (together) are favoured by a high pH value. This is also true for reaction (3), because hydrogen ions are formed on the right side. On the other hand, reaction (4) must be slowed down by a high pH (low hydrogen ion concentration) as one of its products is the hydroxyl $(OH)^-$ ion.

In acid solution, there is a further reaction to be considered:

$$Ni + 2H^+ \longrightarrow Ni^{2+} + H_2 \qquad (6)$$
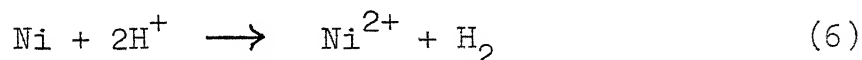
This reaction expresses the fact that the deposited nickel is dissolved, with evolution of hydrogen gas, when the pH is sufficiently low.

The catalyst must be an active dehydrogenation agent as clear from the reaction (1), for this reaction to proceed in forward direction. Numerous metals have been called "catalytic" for this process (for instance: iron, aluminum, copper, gold, silver, etc.).

Considering reaction (3) it can be seen that, in a batch operation the solution will become more and more acidic as the reaction proceeds, until the rate of reaction (6) becomes equal to that of the nickel alloy deposition, and the latter will eventually stop. In order to allow the deposition reaction to proceed continuously or to completion, it is necessary to keep the pH substantially constant. This can be achieved by periodic or continuous addition of a neutralizing chemical, that is, of hydroxyl ions. It can also be promoted by incorporating a buffer in the bath composition (like citric or malic anions).

3.1 Baths:

Practical baths for nickel plating by catalytic chemical reduction are water solutions which consist primarily of a nickel salt to supply nickel ions for reduction to the metal, a salt of hypophosphorous acid (H_3PO_2) which

functions as the reducing agent and a buffer agent to maintain the pH value of the bath in the desired range. The buffer agent in certain cases also acts as a complexing agent to keep nickel ions in solution.

Two general types of baths are in commercial use. The less commonly used type is operated in the pH range from 8 to 10 (alkaline type). The more generally used type is operated in the pH range from 4 to 6 (acid type).

3.1.1 Alkaline Baths:

In practice, these baths plate at a slow rate and are reported to be inconvenient and uneconomical because of the rapid loss of ammonia at the high temperature of operation. Certain advantages are claimed for the alkaline bath.[17]

(i) It is cheaper to operate than acid baths.

(ii) Less critical control is required. Adjustment of pH is made with ammonium hydroxide (diluted 1:1 if hot, or concentrated if cold). A definite colour change is visible when the pH is too low. If the colour fades, sodium hypophosphite is added with the ammoniumhydroxide.

(iii) The deposits are whiter and brighter than from the acid baths.

The characteristics of the alkaline bath are as follows:

2. Hypophosphite concentration

3. Nickel concentration and

4. Phosphite concentration.

The pH level of a bath is related to plating rate and tendency towards spontaneous decomposition. The hypophosphite concentration is important as regards plating rate, efficiency of hypophosphite utilization, and tendency towards spontaneous decomposition. Nickel concentration is associated with hypophosphite concentration relative to plating rate, efficient hypophosphite utilization, and bath stability. As plating proceeds, hypophosphite ion is converted to phosphite ion which has a limited solubility and which may finally precipitate out yielding rough deposits and nuclei for spontaneous decomposition. Thus, phosphite ion concentration is a measure of the extent of bath exhaustion, and impending bath deterioration due to this source can be detected by chemical analysis.

It has been observed that a boiling bath is particularly susceptible to spontaneous decomposition. It is desirable, therefore, to operate at as high a temperature as possible short of boiling. The temperature range over which operation has been reported varies from 70 to 100°C.

CHAPTER 4

DETAILS OF EXPERIMENTAL WORK

4.1 General Electroless Plating Bath:

The general experimental set up used in all the plating work is shown in Figure 1. A double walled glass jacket was used, for electroless plating, in which hot oil at 95°C from a constant temperature bath was circulated. In this way the temperature of the bath was maintained at 90±1°C. All experiments were done under the following common conditions:

(i) Bath temperature maintained at 90±1°C

(ii) Bath composition used:

(a) For nickel plating shown in Table II (Bath No. 4)

(b) For cobalt plating shown in Table I (Bath No. 3)

(iii) Time of plating 30, 60 and 90 minutes

(iv) The powder particles were suspended in the bath by mechanical stirring, in all experiments. The stirring rate, in each case, was varied as per requirements of fluidization of the powder particles.

(v) A constant ratio of substrate weight in grams/volume of plating solution in cc equal to 6/200 was maintained in all experiments.

4.2 Nickel Coating of Alumina Powder:

Since alumina is non-catalytic it is necessary to activate it. Alumina powder of -200 mesh size average was taken. The sequence of activation of alumina powder was as follows:

(i) Degreasing the powder in alkali solution (NaOH 20%)

(ii) Water rinsing the powder to remove alkali.

(iii) Acid dipping, to etch the powder, in a solution of

Hydroflouric acid   50% (v/v)

Sulphuric acid (s.g. 1.84) 50% (v/v)

The acid dipping lasted for 5 minutes.

(iv) Water rinsing to remove the acid completely.

(v) Dipping for two minutes in a sensitizing solution (composition given on page 23).

(vi) Water rinsing.

(vii) Dipping for 3 minutes in an activating solution (composition given on page 23).

(viii) Water rinsing.

The (activated) Pd coated powder was immediately immersed in hot electroless nickel bath. Next the powder was water rinsed after filtration and then dried in the electric oven. In this way the alumina/Ni composite powder was obtained.

4.3 Nickel Coating of Copper Powder:

The copper powder taken was of -325 mesh size average. The following steps were followed to coat this powder:

(i) Degreased **the powder** in alkali solution (NaOH 20%)

(ii) Water rinsed

(iii) Acid dipped, for $\frac{1}{2}$ minute, to etch the powder, in a solution. The composition of the solution is given on page 23.

(iv) Water rinsed

(v) Dipped immediately in hot plating bath.

(vi) Water rinsed and dried the powder. In this way we get the nickel coated copper powder.

4.4 Nickel Coating of Tungsten Powder:

Powder taken was -325 mesh size average. Steps for plating:

(i) Acid dipped for 2 minutes, to etch the powder, in a solution, composition of which is given on page 23.

(ii) Water rinsed

(iii) Dipped the powder after water rinse in sensitizing solution for two minutes (composition given on page 23).

(iv) Water rinsed

(v) Activated the powder by dipping for 5 minutes in activating solution.

(vi) Water rinsed

(vii) Immersed in hot plating bath

(viii) Water rinsed and dried the powder. In this way we got the nickel coated tungsten powder.

4.5 Cobalt Coating of Tungsten Carbide Powder:

Powder taken was -325 mesh size average. The following were the steps for cobalt plating of WC:

(i)   Degreasing the powder in alkali solution (NaOH 20%)

(ii)   Water rinsing the powder to remove the alkali

(iii) Acid dipping, to etch the powder, in acid solution, (given on page 23) for 2 minutes.

(iv)   Water rinsing to remove the acid

(v)   Dipping/hot plating bath.

(vi)   Water rinsing and drying the coated powder. In this way we got the cobalt coated tungsten carbide powder.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Results:

The composite powders obtained by the electoless plating were further examined to find out the effect of coating time on the wt. % Ni or Co deposited, flow rate and apparent density. Hardness of the sintered compacts of the composite powders (Cu/Ni and W/Ni) was also determined. The test procedures adopted for these observation and the results obtained are given below.

5.1.1 Determination of Wt. % Ni and Co Deposited:

The standard gravimetric methods were used for the determination of wt. % Ni and Co.

(i) Nickel Percentage: It was determined by the dimethyl-glyoxime method. One gram sample, of the composite powder, was dissolved in 25 ml. of 1:1 nitric acid. In case of $Al_2O_3/$ Ni and W/Ni only nickel was dissolved in the nitric acid, but in case of Cu/Ni both elements were dissolved. Copper was removed from the solution by passing H_2S gas to precipitate out copper and the excess gas was evaporated by heating (in case of solution made from Cu/Ni composite powder only).

The solution was transferred to a 250 ml. flask, diluted the
solution and washings to the mark and after mixing 50 ml. of
this solution was taken in a beaker. 10 ml. of dimethyl-
glyoxime solution was added to this solution. The solution
was made alkaline by addition of ammonium hydroxide. The
solution was heated at 60°C for two hours. The precipitates
were filtered through a sintered glass crucible of medium
porosity and washed well with water. The precipitates were
dried to constant weight at 150°C. The precipitates were
weighed as nickel dimethylglyoxime. Weight % Ni was
calculated as follows:

$$Wt. \% \; Ni \;\; = \;\; A/B \; x \; 20.32$$

where   A = weight in grams of nickel dimethylglyoxime

       B = weight in grams of sample taken (i.e. 1 gm.)

(ii) <u>Cobalt Percentage</u>: 0.5 gms. of WC/Co composite powder
was dissolved in 20 ml. of concentrated HCl. The solution
was diluted after filtration to 250 ml. 1 gm. of alpha-nitroso-
beta-naphthol was added to 50 ml. of this solution. The red
precipitates of cobaltinitroso-beta-naphthol were allowed to
boil for several minutes. The precipitates were allowed to
stand in a warm place for several hours. The precipitates
were filtered on a Whatman No. 42 paper, using pulp and
were washed several times with hot water. The precipitates

with the paper pulp were placed in a weighed porcelain crucible. They were then dried and ignited in a muffle at a temperature not exceeding 850°C. The contents were cooled in a desiccator and weighed as Co_3O_4. Wt. % of Co was calculated as follows:

$$Wt \% \ Co \ = \ Wt. \ of \ Co_3O_4 \ x \ 0.7342$$

Results of the above observations are given in Table III and Figures 3, 4 and 5.

TABLE III

Time of coating in minutes	Wt. % Ni in Al_2O_3/Ni	Wt. % Ni in Cu/Ni	Wt. % Ni in W/Ni	Wt. % Co in WC/Co
30	5.85	4.5	2.50	7.1
60	6.45	5.6	3.30	8.0
90	6.95	6.0	3.95	8.2

5.1.2 Flow Rate and Apparent Density Measurement:

ASTM Standard No. B213-46T, powder flowmeter (sketched in Figure 2) was used to determine the flow rate and apparent density.

(i) Flow Rate: 50 gms. of the composite powder were taken in the funnel and allowed to have a gravity fall in the

density cup, kept at a distance of 1 inch from the bottom of
the funnel. The time of fall was noted in seconds. This
gives the flow rate of the powder in sec./50 gms.

(ii) <u>Apparent Density</u>: The bottom hole of the funnel was
closed with the finger. The funnel was filled completely
with the composite powder. The powder was allowed to fall
from the funnel into the density cup, placed at a distance
of 1 inch from the bottom of the funnel, by removing the
finger. The density cup was completely filled with the
powder and the powder levelled off flush with the top of the
cup. Weighed the cup's contents. Volume of the cup was
known. The apparent density is calculated as follows:

$$\text{Apparent density} = \frac{\text{Weight of powder in the cup in gms.}}{\text{Volume of the cup in cc.}}$$

The effect of plating time (i.e. plating thickness) on the
flow rate and the apparent density of different composite
powders was studied (results given in Table IV and Figures
6, 7, 8 and 9).

TABLE IV

Composites	Flow rate sec./ 50 gms.			Apparent density g/cc.		
	Coating time in minutes					
	30	60	90	30	60	90
Al_2O_3/Ni	124.0	122.0	118.0	0.85	0.88	0.89
Cu/Ni	87.0	83.0	81.0	1.46	1.49	1.50
W/Ni	27.5	26.9	25.0	4.53	4.88	5.07
WC/Co	20.8	20.0	18.1	5.50	5.57	5.63

Each one of these readings is a mean of 5 readings observed.

5.1.3 Hardness Measurement:

The powders were compacted on a hydrolic press using a 3/8" dia. cylindrical split die at a pressure of 21×10^4 lbs/in^2. The compacts were then sintered at 700, 800 and 900°C, using an electric resistance furnace, in a vacuum of 300 microns. The sintering time for Cu/Ni and W/Ni composite powder compacts was one hour and two hours respectively.

The hardness measurements were made on Vicker's hardness tester using, for indentation, $2\frac{1}{2}$ Kg weight for Cu/Ni compacts and 10 Kg weight for W/Ni compacts. The results thus obtained are tabulated in Table V and the trend shown in Figure 10.

TABLE V

Time of coating in minutes	Hardness VPN					
	Sintering Temperature °C					
	Cu/Ni Composite			W/Ni Composite		
	700	800	900	700	800	900
30	90.8	94.9	102	300	322	336
60	97.6	110.0	133	220	236	276
90	99.4	120.0	143	200	227	247

5.1.4 Micrographs:

Some of the powder particles were sprayed on a glass slide. The slide was tapped to reduce the clustering of the particles. It was then observed under the microscope. The micrographs are shown in M_1, M_2, M_3 and M_4.

Some of the nickel coated alumina composite powder particles were mixed with the mounting powder and were mounted on this material by applying heat and pressure. The surface was polished carefully so that no particle was removed from the mounting. Then the cross-section of the particle was observed under the microscope (given in M_1).

The surfaces of the samples (sintered compacts of Cu/Ni composite powders) were polished and etched with $FeCl_3$ solution. The structure was observed under the microscope (given in M_2).

5.2 General Discussion:

5.2.1 Flow Rate:

It has been established by several workers[4] that the flow rate of the composite powders is effected by

(i) the specific gravity of the components,

(ii) the particle shape,

(iii) the size of the core,

(iv) the thickness of the coating, and

(v) the coefficient of inter-particle friction.

As seen in Figures 6 and 7, the time needed for the
same flow to occur has decreased as the coating thickness
increases, in every composite powder. This shows an improve-
ment in the flow characteristics of the composite. The
increasing trend of the flow rate with increasing coating
thickness may be explained as follows:

The average shape of the particles and the average
size of the core is same in every composite powder, so there
may not be much effect of these factors on the flow rate.
As the coating thickness increases, in case of Al_2O_3/Ni, the
specific gravity of the combination increases. It is known
that as specific gravity, of the same size of the particles,
increases the time to gravity fall decreases. Based on this
fact the increasing trend of the flow rate is obvious. But
in case of WC/Co, the specific gravity of the combination is
decreasing still the flow rate is increasing. This is not
in agreement with this fact. So there may be little effect
of specific gravity.

The resistance against flow depends primarily on
the regions in which one particle hampers the free movement
of other particles, either by direct contact or indirectly.
This is mainly determined by the coefficient of inter-particle

friction. It is supposed that as the time of coating increases, the coating becomes more and more uniform on each particle i.e. with increase in coating time the particle is getting more and more completely covered with the plating material. The more uniform is the coating, there is the corresponding decrease in the coefficient of inter-particle friction. Lesser the coefficient of inter-particle friction more the flow rate. The increasing trend in flow rate may be due to this fact.

5.2.2 Apparent Density:

The apparent density is greatly influenced by a number of factors, one of which is the packing mode and the other is derived from the nature or condition of the metal. The factors affecting packing mode are (a) the particle shape, and (b) the particle size. Other factors influencing the apparent density include (1) manner of packing the container, (2) shape and size of the container, (3) absolute unit incumbent weight of powder, (4) electrostatic forces, (5) surface conditions, and (6) specific properties of the powder e.g. hardness.

Due to the complexities of the above factors it is difficult to come to any conclusion regarding the increasing trend of the apparent density curve. Some additional indirect experiments should throw some light on the possible reasons of such a trend.

5.2.3 Weight Percent Nickel or Cobalt Deposited:

As seen in the Figures 3, 4 and 5 the wt. % Ni or Co deposited is increasing at a steeper rate in the initial periods. But for larger times the gradient is observed to be reduced. Due to the limited number of experiments taken up in the present work it is not clear whether the % Ni or Co deposited has reached a saturation value or not. But, many workers[7] have observed the flattening of the curve beyond a certain "saturation time".

The plating rate is controlled by the ratio of nickel or cobalt ions to hypophosphite ions in the bath, at an optimum absolute hypophosphite concentration. It has been shown[16] that there exists an optimum range of this ratio at which the best plating results are obtained. As an example in case of acid bath for Ni coating this optimum ratio lies in the range 0.25 to 0.6. If the ratio is greater a poor rate of deposition results and the plating stops almost beyond that point.

The trend of the curves may be explained on the basis of this fact. The ratio of ions in the solution are within the range in the initial periods. The ratio increases with time, because of the consumption of hypophosphite ions for reduction of Ni ions. Hence the plating rate decreases and stops almost beyond the saturation time and hence the flattening of the curve after that time.

5.2.4 <u>Hardness</u>:

Hardness of copper-nickel alloy will increase with increase in nickel %age. The increasing trend in hardness of sintered Cu/Ni composite powder compacts can be explained on this basis. Hardness is also increasing with sintering temperature. Complete sintering of the compact depends upon the sintering time and temperature. Here time is kept constant and temperature varied. As the sintering temperature is increasing, the completion of sintering is also approaching. It is also clear from the micrographs of the compacts (M_2) sintered at 700, 800 and 900°C. The grain boundary formation is observed in case of compact sintered at 900°C and not in the other two cases. Hardness is more in case of the completely sintered compact than the less sintered compact.

Hardness is decreasing with increase in Ni percentage in W/Ni alloy, which is obvious because nickel is less hard than W and also at very low percentages of Ni no intermetallic compound formation is there (as seen from the equilibrium diagram of W-Ni). But with the increase in sintering temperature the hardness is increasing which can also be explained on the basis of completion of sintering (as in case of Cu/Ni).

CHAPTER 6

CONCLUSIONS

On the basis of results and discussion presented
in the preceding chapter the following conclusions can be
drawn.

1. Electroless plating method is quite suitable for
    coating nickel and cobalt on tungsten, copper, alumina
    and tungsten carbide.

2. The coating thickness increases with coating time.

3. Flow rate and apparent density increase with coating
    time.

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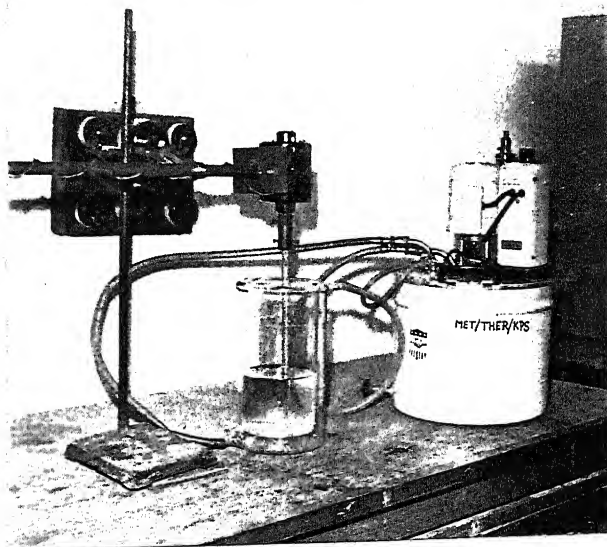
FIGURE : 1 . Experimental set up for electroless plating.

60°

$\frac{1}{8}$ inch

FUNNEL

$\frac{1}{10}$ inch

DENSITY CUP
25 cc.
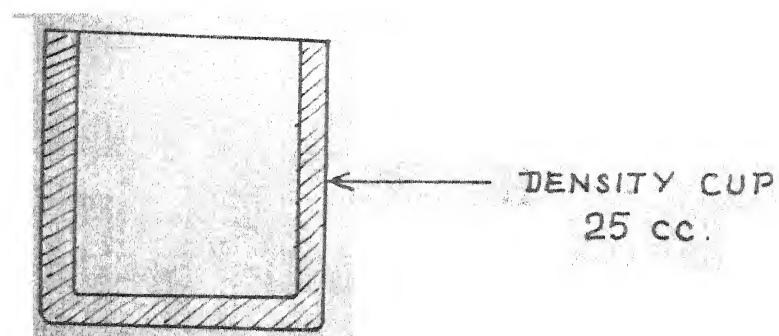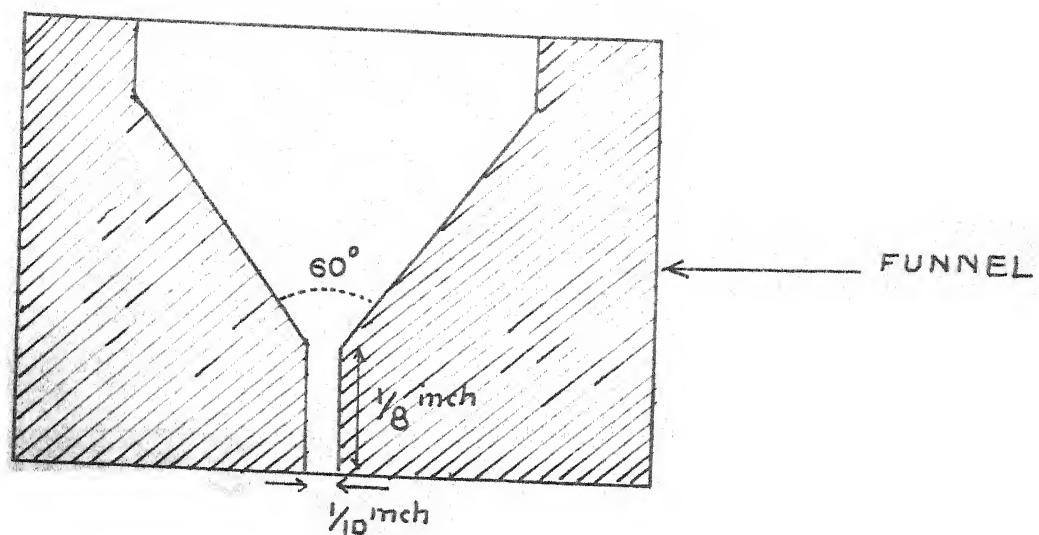
FIG. 2 : FLOWRATE AND APPARANT
DENSITY MEASURING CUP.
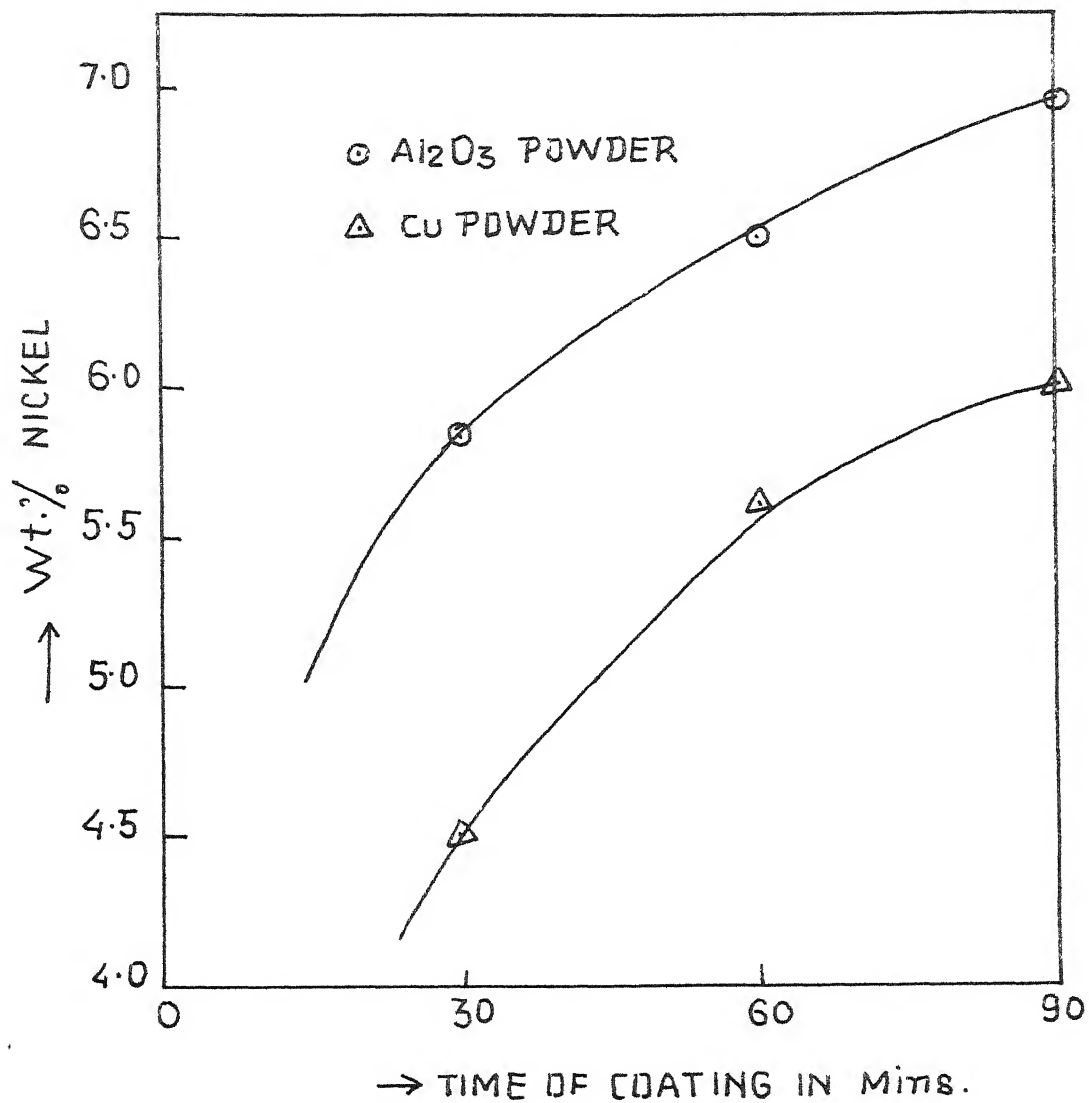
FIG. 3 : EFFECT OF COATING TIME ON THE Wt.% NICKEL COATED ONTO Al_2O_3 AND Cu POWDERS.
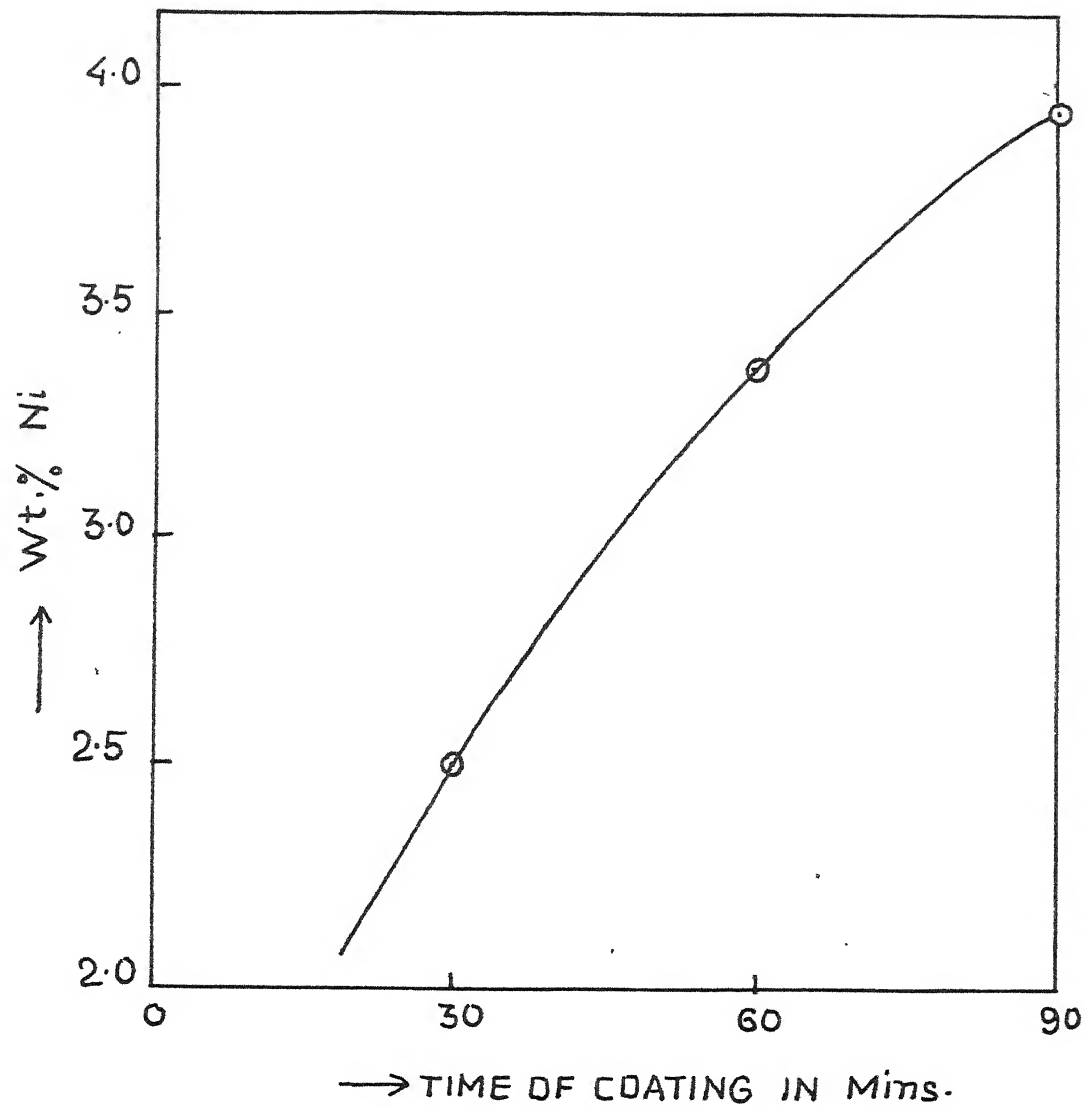
FIG. 4 : EFFECT OF COATING TIME ON THE
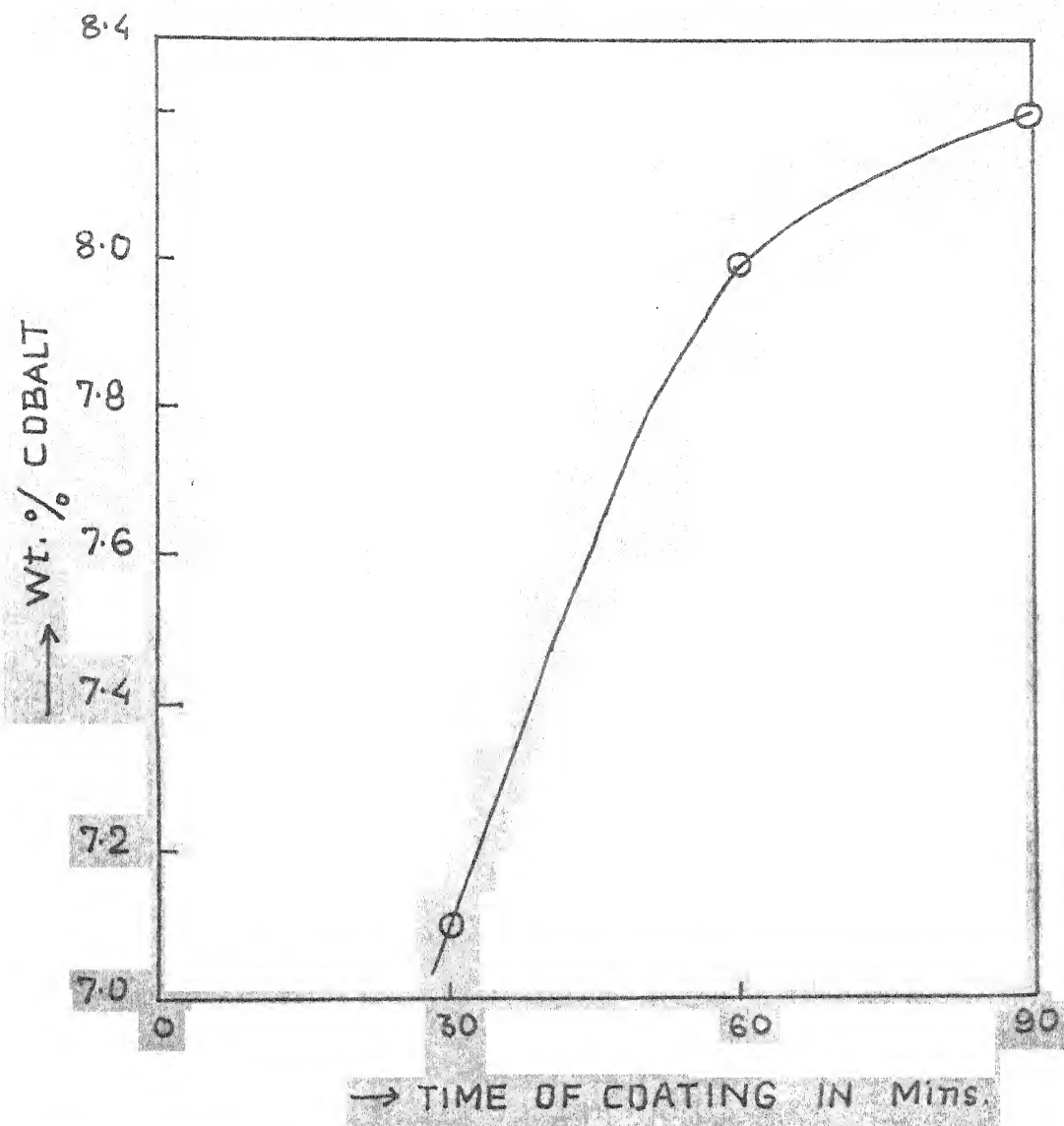Wt.% NICKEL COATED ONTO W
POWDER.

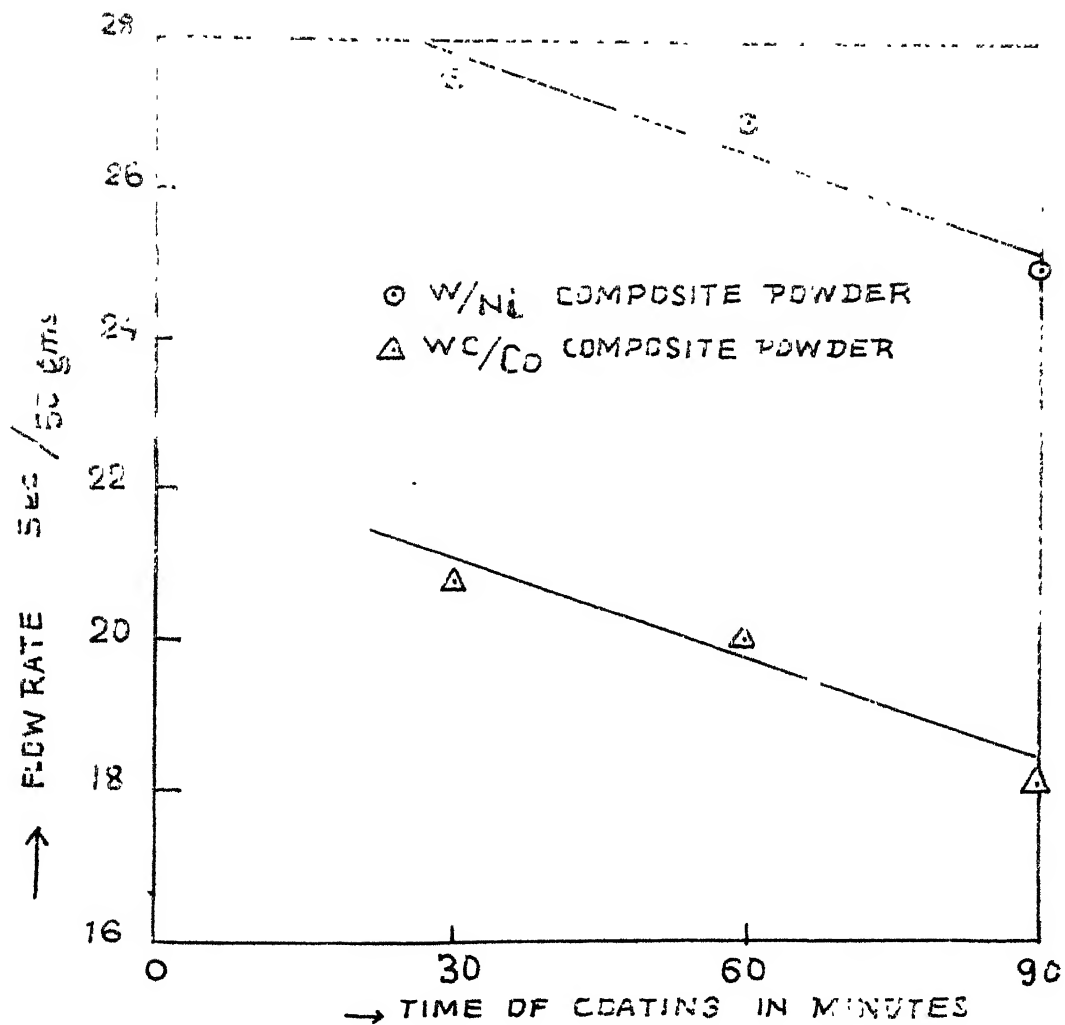FIG. 5: EFFECT OF COATING TIME ON Wt.% COBALT COATED ONTO Wc POWDER.

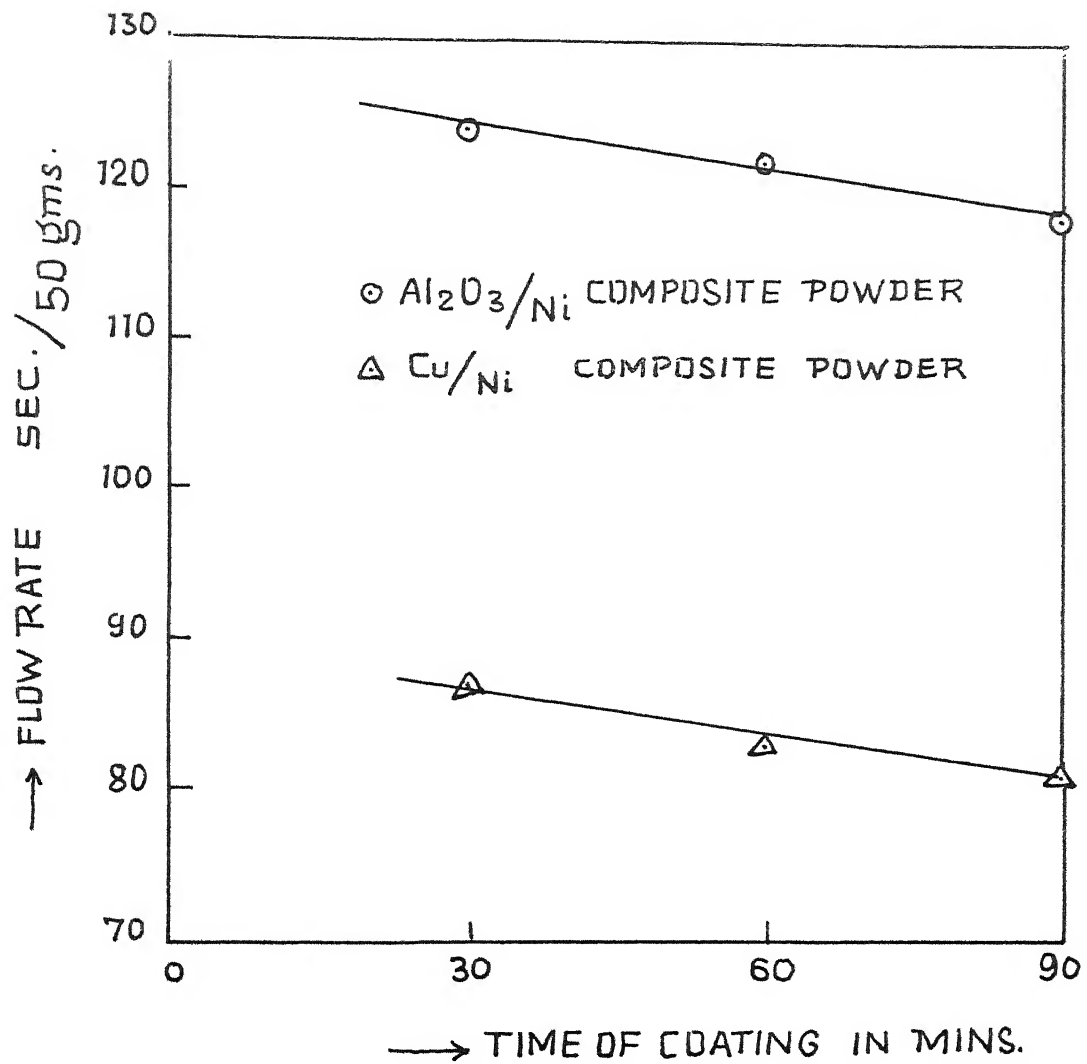FIG. 6 : EFFECT OF COATING TIME ON FLOW
RATE OF THE Wc AND W POWDERS.

Fig. 7: EFFECT OF COATING TIME ON FLOW RATE OF THE Al₂O₃ AND Cu POWDERS.
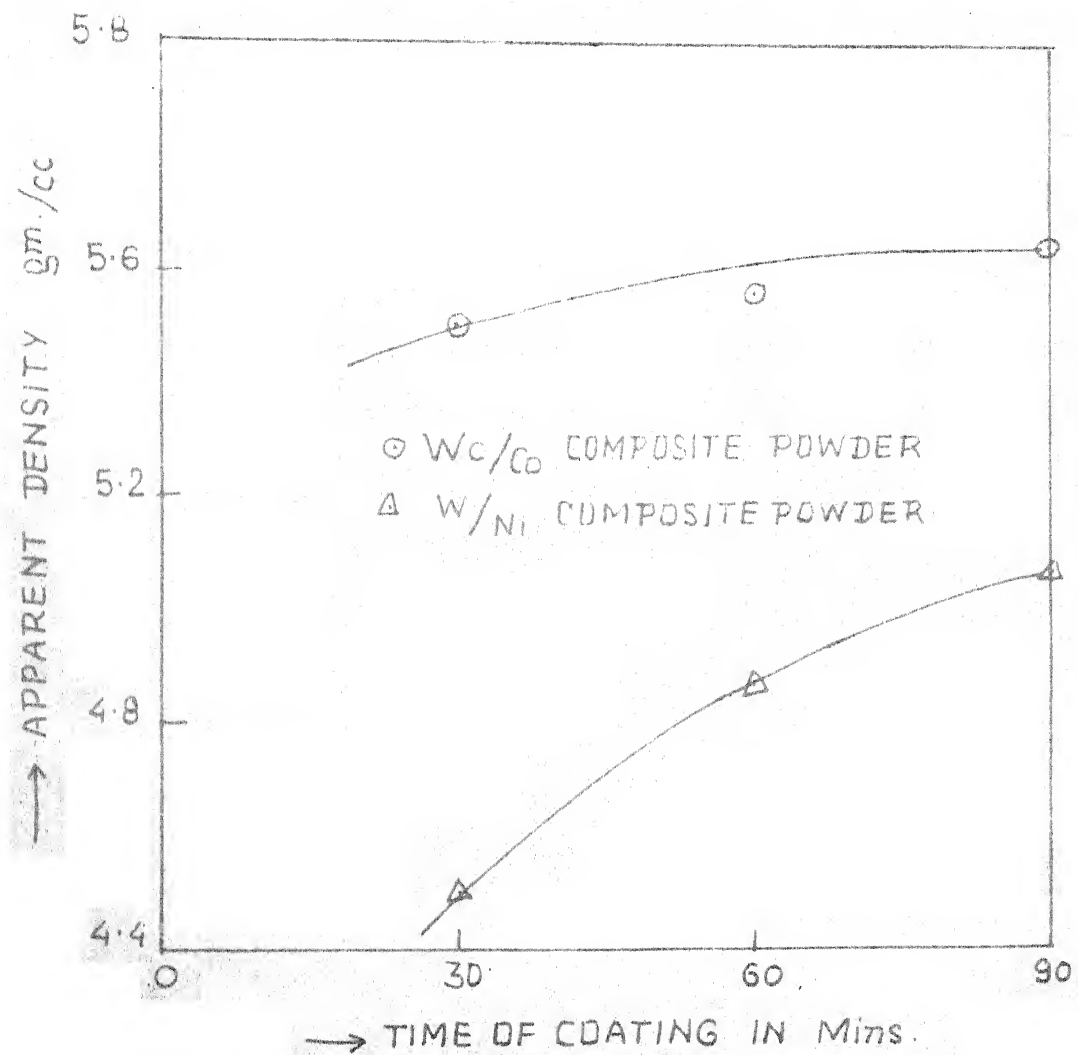
FIG. 8 : EFFECT OF COATING TIME ON THE APPARENT DENSITIES OF Wc AND W POWDERS.
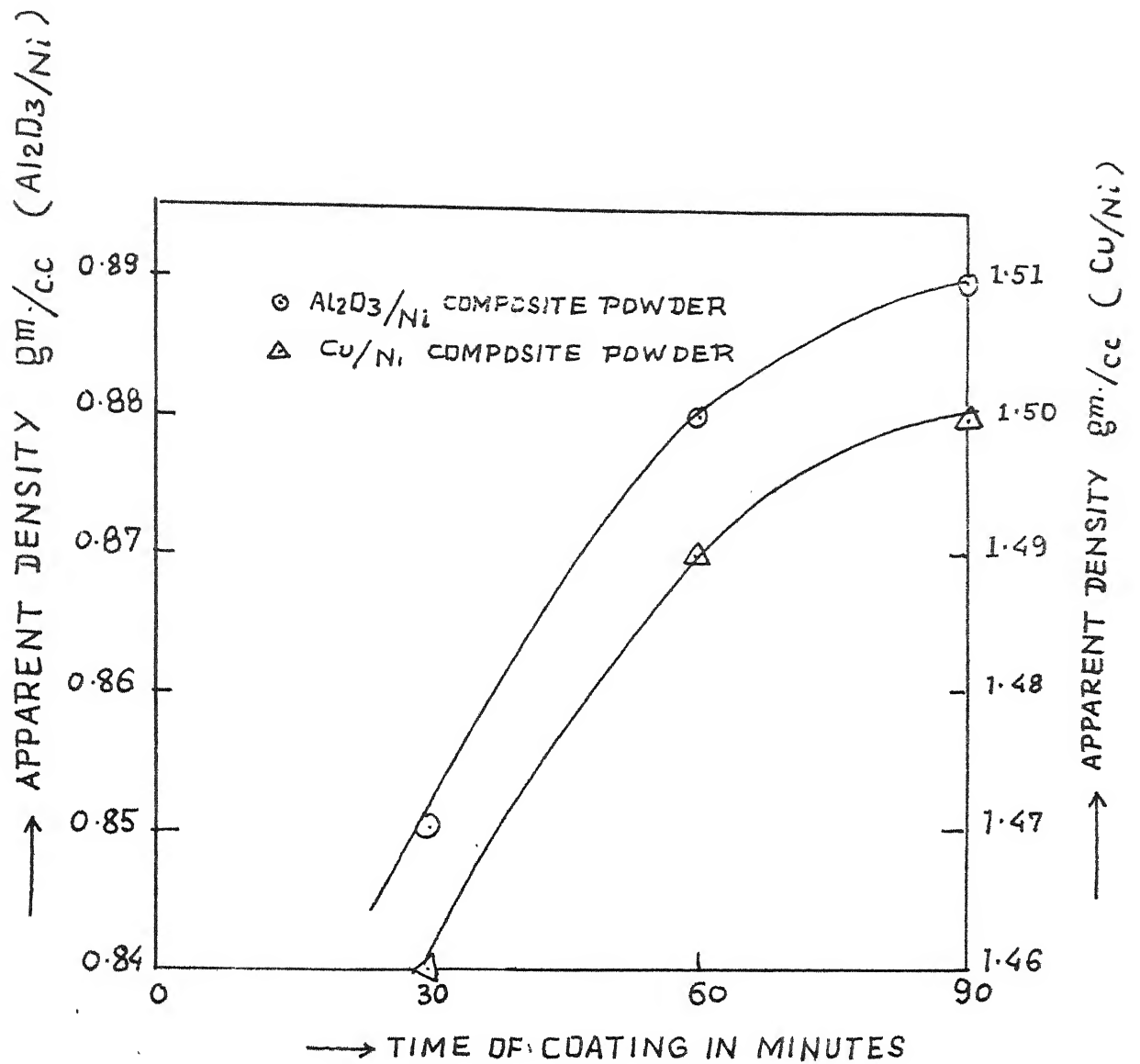
FIG. 9 : EFFECT OF COATING TIME ON THE
APPARENT DENSITIES OF Al₂O₃
AND Cu POWDERS.
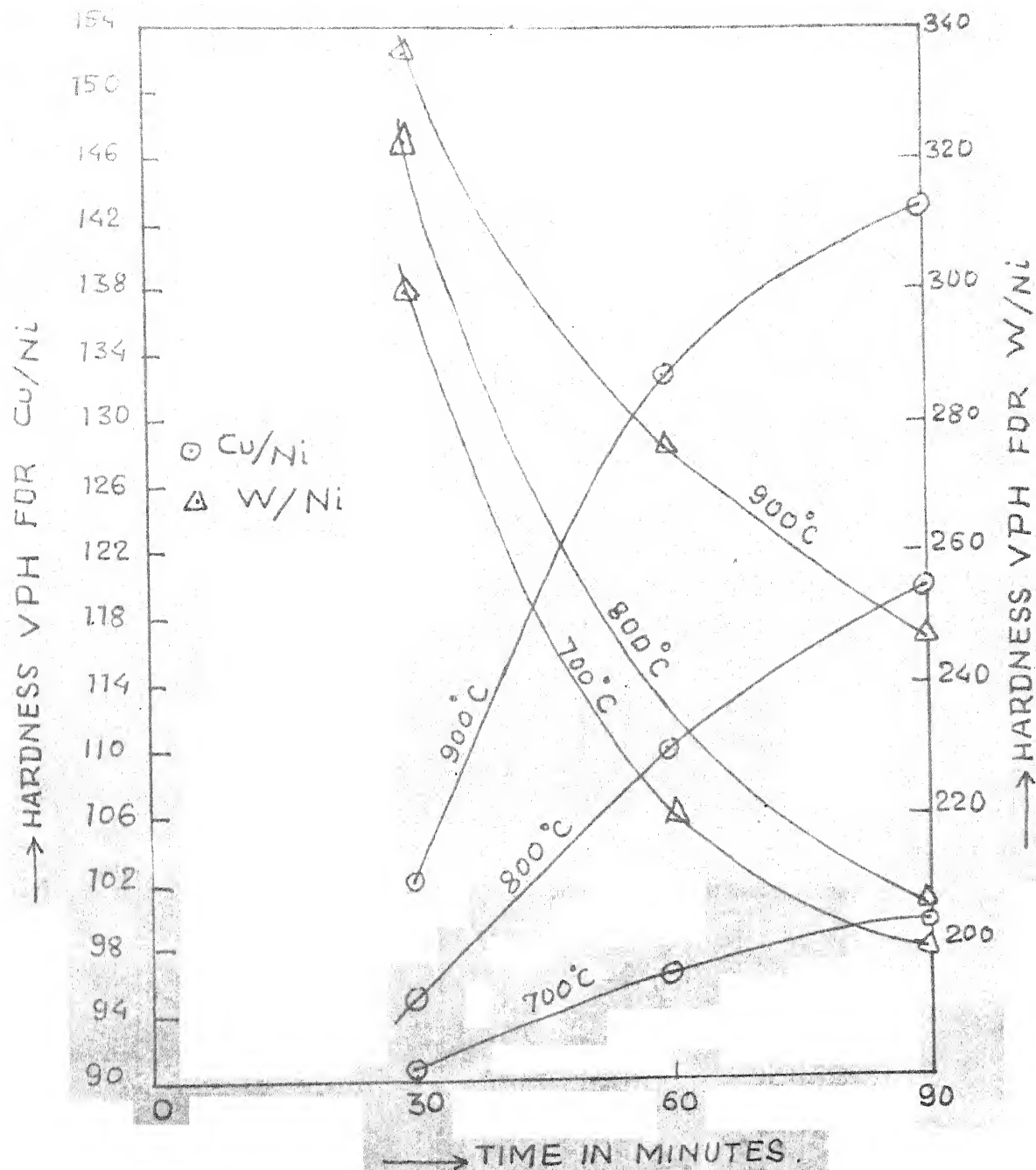
FIG. 10 : EFFECT OF COATING TIME (i.e INCREASE IN COATING THICKNESS) ON THE HARDNESS OF SINTERER COMPACTS OF Cu/Ni AND W/Ni COMPOSITE POWDERS

SINTERING TEMPARATURES ARE 700°C 800°C AND 900°C

M1. Alumina/Ni composite powder particles.   300X
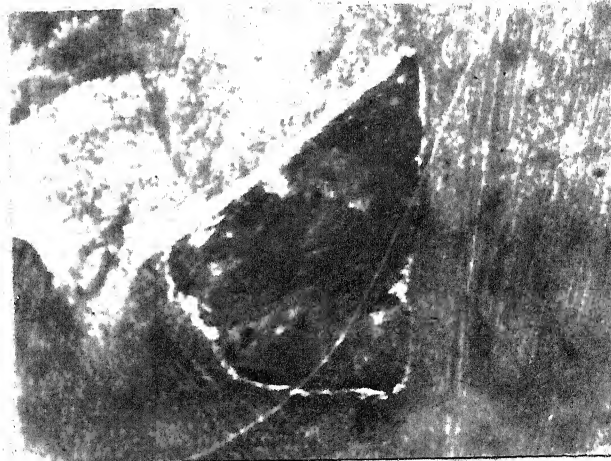
M1. Cross-section of Ni coated alumina particle.   600X
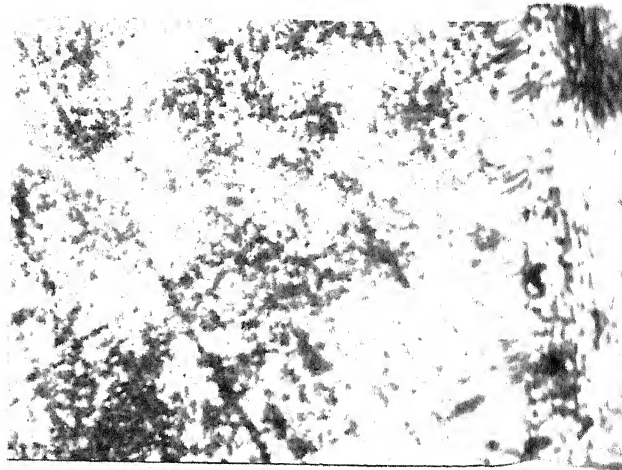
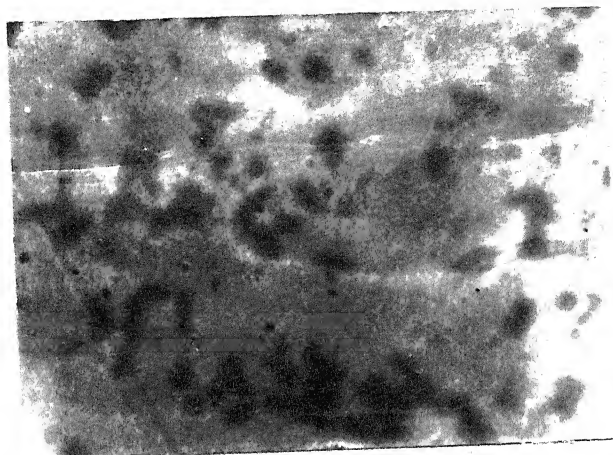M2. Sintered compact of Cu/Ni composite powder, sintered at 700°C, 1000
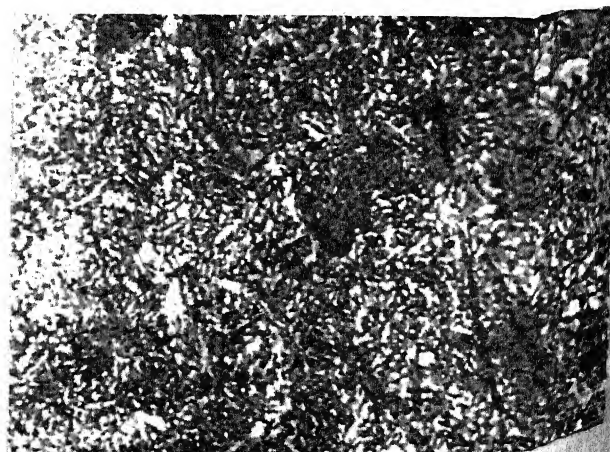
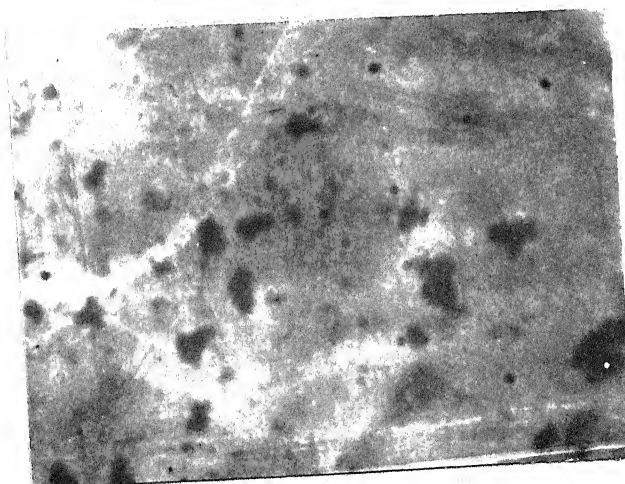M2. Sintered compact of Cu/Ni composite powder, sintered at 800°C.

M2. Sintered compact of Cu/Ni composite powder, sintered at 900°C. 100X
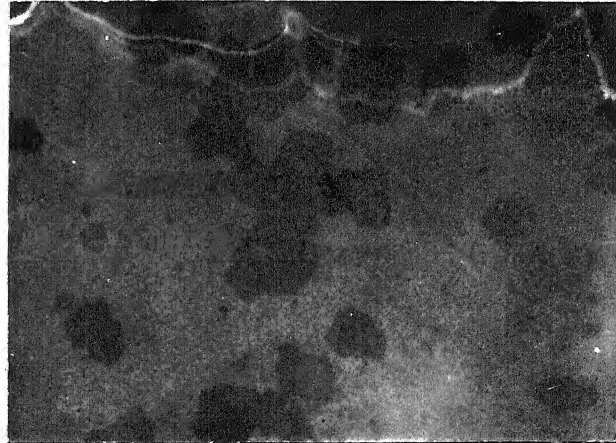
M2. Cu/Ni composite powder particles. 300X
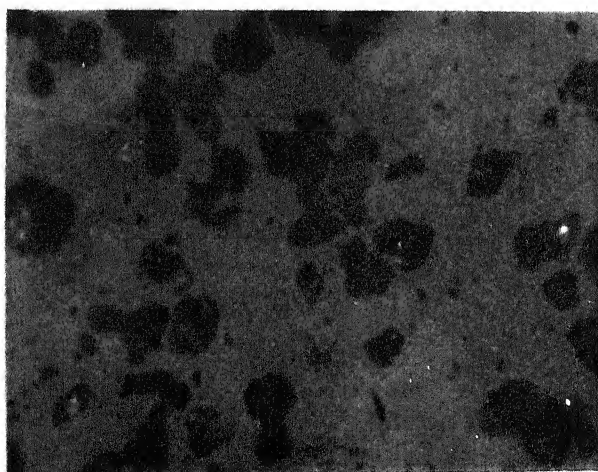
M3. W/Ni composite powder particles,(Plating time 30 min.) 100X

M3. W/Ni composite powder particles (Plating time 60 min.) 100X

M3.   W/Ni composite powder particles (Plating time 90 min.) 100X

M4.   WC/Co composite powder particles.   300X

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